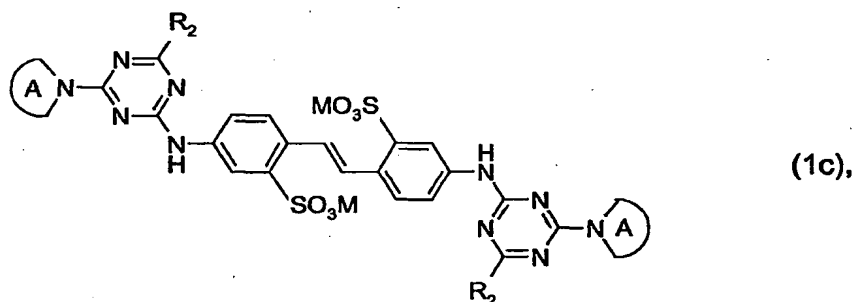
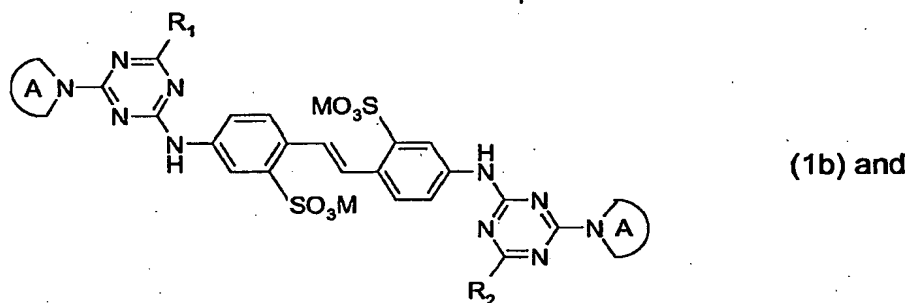
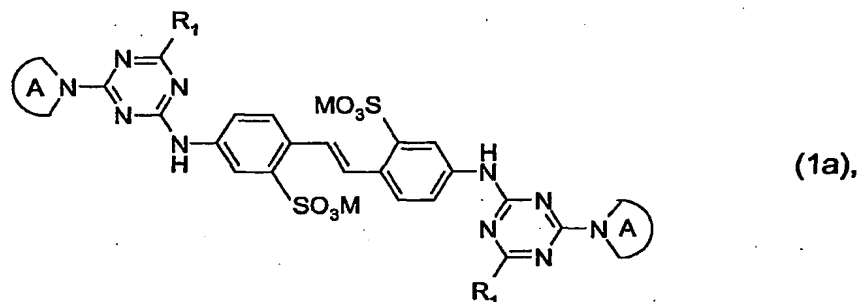


Claims

1. A fluorescent whitening agent, which comprises a mixture of compounds of the formulae



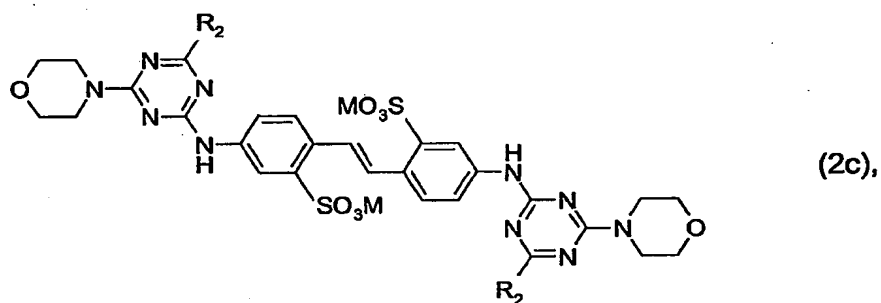
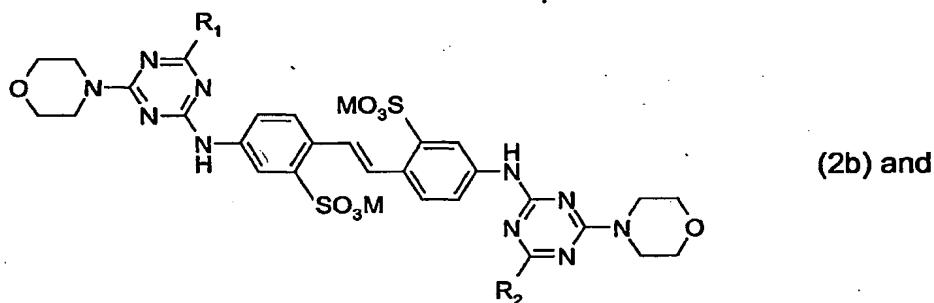
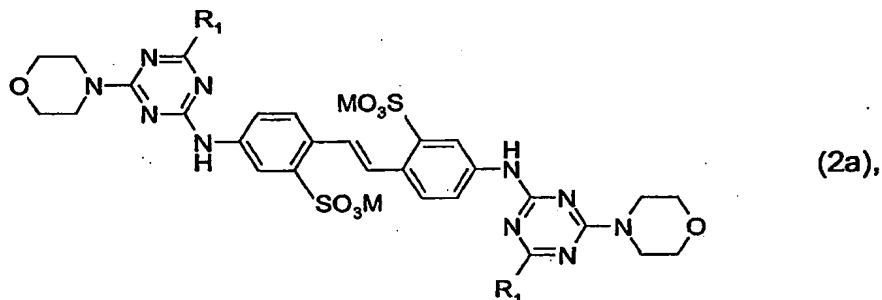
in which

R₁ and R₂ are different and each represents -NH₂, -NHC₁-C₄alkyl, -N(C₁-C₄alkyl)₂, -NHC₂-C₄ hydroxyalkyl, -N(C₂-C₄hydroxyalkyl)₂, -N(C₁-C₄alkyl)(C₂-C₄ hydroxyalkyl), a morpholino residue or an amino acid or an amino acid amide residue from which a hydrogen atom has been removed from the amino group, each of the rings designated as A represent a 5- or 6-membered saturated heterocycle, which may contain one further heteroatom and

M represents hydrogen, an alkali metal atom, ammonium or a cation formed from an amine.

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2. A fluorescent whitening agent, according to claim 1, which comprises a mixture of compounds of the formulae



in which

R₁, R₂ and M are as defined in claim 1.

3. A composition according to claims 1 or 2, in which the aliphatic amino acid or amino acid amide residue is of the formula



in which each

R₃ and R₃, independently, represent hydrogen or a group having the formula

$-\text{CHR}_4\text{R}_5$ in which

R₄ and R₅, independently, are hydrogen or C₁-C₄alkyl optionally substituted by one or two substituents selected from the group consisting of hydroxy, thio, methylthio, amino, carboxy,

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sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β -indolyl, β -imidazolyl and $\text{NH}=\text{C}(\text{NH}_2)\text{NH}-$.

4. A composition according to claim 3, in which residues R_1 and/or R_2 are derived from glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β -indolylalanine), histidine (β -imidazolylalanine), α -aminobutyric acid, methionine, valine (α -aminoisovaleric acid), norvaline, leucine (α -aminoisocaproic acid), isoleucine (α -amino- β -methylvaleric acid), norleucine (α -amino-n-caproic acid), arginine, ornithine (α,δ -diaminovaleric acid), lysine (α,ϵ -diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α -aminoglutaric acid), threonine, hydroxyglutamic acid and taurine, as well as mixtures and optical isomers thereof, or from iminodiacetic acid or from N-(propionamido)-N-(2-hydroxyethyl)amine.

5. A composition according to claims 1 or 2, in which

R_1 and R_2 represent $-\text{N}(\text{C}_1\text{-C}_4\text{alkyl})_2$, $-\text{NHC}_2\text{-C}_4\text{hydroxyalkyl}$, $-\text{N}(\text{C}_2\text{-C}_4\text{hydroxyalkyl})_2$, $-\text{N}(\text{C}_1\text{-C}_4\text{alkyl})(\text{C}_2\text{-C}_4\text{hydroxyalkyl})$, a morpholino residue or a residue derived from glycine, sarcosine, taurine, glutamic acid, aspartic acid, iminodiacetic acid or from N-(propionamido)-N-(2-hydroxyethyl)amine.

6. A composition according to claim 5 in which

R_1 represents a mono-(2-hydroxyethyl)amino, a di-(2-hydroxyethyl)amino, a di-(2-hydroxypropyl)amino, a diethylamino, an N-(2-hydroxyethyl)-N-methylamino, a morpholino, an N-(propionamido)-N-(2-hydroxyethyl)amino or a sarcosine residue and R_2 represents an aspartic acid or a glycine residue.

7. A composition according to any one of claims 1 to 6, in which

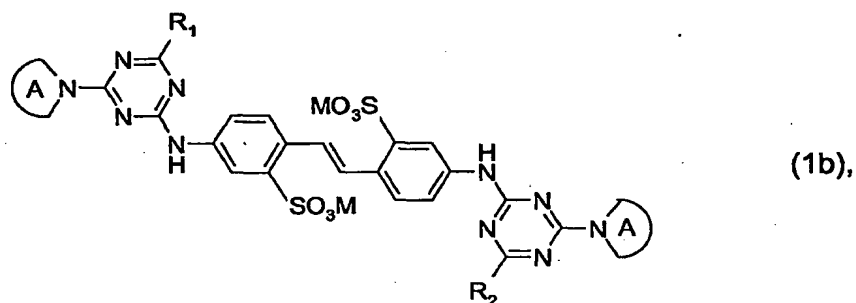
M represents hydrogen, lithium, potassium, sodium, ammonium, mono-, di-, tri- or tetra- $\text{C}_1\text{-C}_4\text{alkylammonium}$, mono-, di- or tri- $\text{C}_1\text{-C}_4\text{hydroxyalkylammonium}$ or ammonium that is di- or tri-substituted with a mixture of $\text{C}_1\text{-C}_4\text{alkyl}$ and $\text{C}_1\text{-C}_4\text{hydroxyalkyl}$ groups.

8. A composition according to claim 7, in which

M represents hydrogen, potassium or sodium.

9. A process for the preparation of the compound mixture of formulae (1a), (1b) and (1c) by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'-disulphonic acid, an appropriate heterocyclic compound, an amino compound R₁H and an amino compound R₂H, or, alternatively a mixture of amino compounds R₁H and R₂H, R₁ and R₂ being as defined in claim 1.

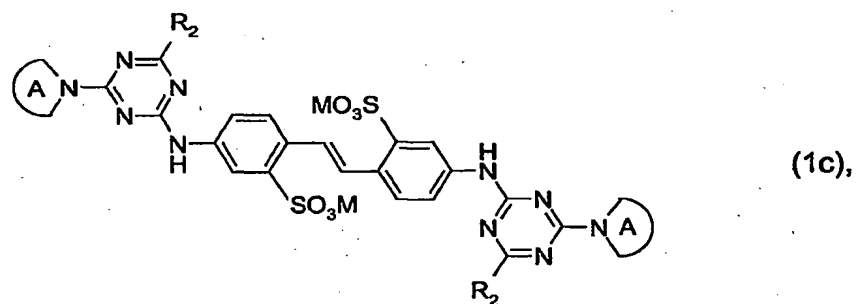
10. A compound of the formula



in which

R₁, R₂, A and M are as defined in claim 1.

11. A compound of formula



in which

R₂ is an amino acid or amino acid derivative from which a hydrogen atom has been removed from the amino group, whereby the residue is derived from alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine (β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-

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diaminovaleric acid), lysine (α,ϵ -diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α -aminoglutaric acid), threonine or hydroxyglutamic acid, as well as mixtures and optical isomers thereof, or from iminodiacetic acid or from N-(propionamido)-N-(2-hydroxyethyl)amine or the corresponding propionic acid, the heterocyclic ring A and the symbol M being as defined in claim 1.

12. Use of a composition, which contains water, a fluorescent whitening agent, which comprises a mixture of the compounds (1a), (1b) and (1c), according to any one of claims 1 to 8, a compound of formula (1b) according to claim 10 or a compound of formula (1c) according to claim 11 and, optionally, auxiliaries, for whitening synthetic or natural organic materials.

13. Use according to claim 12 as optical brightening agents for paper in pulp, size-press, metering press or coating applications.

14. Paper, which has been optically brightened by the compound mixture of formulae (1a), (1b) and (1c) according to any one of claims 1 to 8, a compound of formula (1b) according to claim 10 or a compound of formula (1c) according to claim 11.

15. Use according to claim 12, for increasing the Sun Protection Factor (SPF) rating or for the fluorescent whitening of a textile fibre materials.

16. A textile fabric produced from a fibre treated with the compound mixture of formulae (1a), (1b) and (1c) according to any one of claims 1 to 8, a compound of formula (1b) according to claim 10 or a compound of formula (1c) according to claim 11.